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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Polymer Moulding Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polymer moulding compositions.

According to the present invention we provide a polymer moulding composition comprising at least 55% by weight of propylene monomer units, monomer units of a linear 1-olefine having from 4 to 18 carbon atoms (hereinafter referred to as the second component) in amount of up to 35% by weight and having dispersed throughout the composition polymer units of an α -olefine (hereinafter referred to as the third component) whereof the homopolymer has a crystalline melting point above 180° and preferably above 260°C which is present in an amount of up to 10% and preferably less than 5% by weight. Preferably the composition contains at least 2% by weight of the second component.

We further provide a polymerisation process which comprises bringing propylene, the second component and the third component into contact with an α -olefine polymerisation catalyst and recovering a solid copolymer composition comprising at least 55% by weight of propylene monomer units, up to 35% by weight of monomer units of the second component and polymer units of the third component in an amount of up to 10% by weight.

The compositions of our invention in general have improved transparency compared with polypropylene homopolymer. In some cases the transparency is very much improved;

for example, most of our compositions have a light transmission of at least 40%, and certain of the compositions are found to have a light transmission of 80%, in 1/16" section. The average spherulite size of mouldings made from our compositions is in general below 5 μ , and frequently, in quenched mouldings, below 1 μ . Our compositions can also show better moulding behaviour than polypropylene homopolymer, voids and sinking being reduced.

Our physical properties of the polymers, e.g. stiffness and toughness, are dependent on the relative proportions of the three monomer components in the composition and the manner in which they have been incorporated. In general, the flexibility of the composition increases with increasing content of second component.

Butene-1 is particularly suitable for use as second component on account of its cheapness and ready availability; octene-1 also gives good results. As third component 3-methyl pentene-1, 4,4-dimethylpentene-1 (both giving homopolymers which melt above 350°C), vinylcyclohexane (homopolymer melts at 342°C) and 3-methyl butene-1 (homopolymer melts at 310°C) are particularly suitable.

Mixtures of two or more second components or two or more third components, or both, may be used; it is also possible for small quantities of ethylene units, e.g. up to 10% by weight, to be incorporated in the copolymer composition.

The function of the dispersed polymer units of the third component is to reduce the average spherulite size of the composition when moulded and hence improve its moulding and optical properties over those of polymer compositions containing propylene and the second component only. Surprisingly little

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of the third component is sufficient for this purpose. Infra-red analysis of copolymer compositions is not effective where the concentration of the third component is below about 0.5 to 1% by weight; yet compositions with improved properties may be obtained when third component has been present during the polymerisation reaction in amounts insufficient to give 0.5% by weight of third component in the final product. It will be seen, therefore, that it is not practicable to give a quantitative lower limit to the amount of third component required in the composition.

The manufacture of compositions according to the invention may be carried out in a wide variety of ways. Generally, to form polymer units of the third component this must be polymerised for a period in substantial absence of other monomers. This may be done before propylene or the second component have been polymerised, or after the polymerisation of either or both; it can be done more than once, though no advantage is found in so doing. It is particularly convenient to polymerise the third component on a small scale before any or the bulk of the other components have been polymerised. This is because of the slow polymerisation rate of the third component compared with the other two and the small amount of it required in the final copolymer composition; a large catalyst concentration may be used to increase polymerisation rate, the small scale of the process makes a longer polymerisation time more economic, and recovery of unreacted third component (if any) is easier on a small scale and in the absence of other monomers. However, another possible way of working the invention is to add all three components to the catalyst together, and polymerise for an extended time. In this way the third component polymerises slowest and so is the last monomer to be exhausted; thus in the last stages of polymerisation third component polymer units are being formed in the substantial absence of other monomers.

It is convenient to use a stereospecific catalyst for the polymerisation. By a "stereospecific catalyst" we mean one which under equivalent conditions will polymerise propylene in the absence of other monomers to solid polypropylene which is at least 70% insoluble in boiling n-heptane. Numerous catalysts which will do this are known to the art — for example, many suitable catalysts are described in Gaylord and Mark "Linear and Stereoregular Addition Polymers", Interscience, 1959. Generally they comprise a compound of a transition metal from Groups IV to VI of the Periodic Table activated by an organometallic compound or metal hydride. Most widely used are those catalysts which comprise titanium trichloride activated by an organo-aluminium compound, e.g. an aluminium trialkyl or alkyl halide in which each

alkyl group contains from 1 to 8 carbon atoms. We prefer to use the material obtained by reacting titanium tetrachloride with aluminium alkyl sesquichloride in a purified alkane solution at about 0°C preferably by adding a solution of the sesquichloride gradually (e.g. dropwise) to a solution of titanium tetrachloride, using an aluminium/titanium molar ratio in the range 0.4—4.0. The product so obtained may be washed with hydrocarbon and/or submitted to one or more heat treatments between 60° and 150°C before use. As activator for this material we prefer to use dialkyl aluminium chloride.

Polymerisation is carried out in the absence of air and water or in the presence of only limited amounts of these since in other than small concentrations both air and water deactivate the catalyst. Conveniently an inert hydrocarbon diluent is used as polymerisation medium. Nitrogen is often used to purge the apparatus beforehand. Super-atmospheric pressure may be used. Hydrogen may be used to lower the molecular weight and raise the melt flow index of the copolymer composition.

Free-flowing slurries of polymer in diluent are easier to handle and deash than polymer solutions or sticky, viscous gels. Slurries are formed more readily at lower temperatures; copolymerisation has a tendency to form gels. We find that conditions at the beginning of polymerisation are the most important in determining whether or not slurries are formed. We therefore prefer initially to homopolymerise one of the components in the absence of any other monomer, preferably at a relatively low temperature, e.g. below 30°C, until at least 1% by weight of the final polymer composition has been formed. In polymerisations of this type there is a reduced tendency for solutions or gels to form, even when the temperature is raised at a later stage in the polymerisation.

It may be convenient to form up to 10% by weight of the total amount of the copolymer composition in this way before any other component is added. The preferred component to use at the beginning of polymerisation in this way is propylene; a particularly convenient method of carrying out the process of our invention comprises initially homopolymerising propylene and thereafter homopolymerising the third component in the presence of a high concentration of catalyst, adding diluent to lower the catalyst concentration, and subsequently polymerising propylene and the second component. The term "pre-treated catalyst" is used hereafter to describe a catalyst which has been treated with one or more monomers at high catalyst concentration and subsequently used at lower catalyst concentration for a further polymerisation.

Aqueous deashing, e.g. by treating the polymer slurry with 1—5% by volume of an alcohol and then washing with water; may be

used, but to obtain copolymer compositions of the highest transparency, de-ashing is preferably carried out under substantially anhydrous conditions using dry reagents. Non-
 5 aqueous deashing may conveniently be carried out in two main ways. One is by adding a small quantity of deashing reagent to the reaction mixture (if the reaction mixture is a
 10 solution this will generally serve to precipitate polymer from it), digesting for a period at moderate temperature, e.g. between 20 and 60°C, followed by filtration and washing with more deashing reagent or hydrocarbon or mix-
 15 tures of the two. The other is first to separate all or most of the polymerisation diluent from the polymer produced and then to re-slurry the polymer one or more times in deashing reagent. In the first process the most suitable
 25 types of deashing reagent are the hydrocarbon-miscible alcohols such as isopropanol, n-butanol/isobutanol or the higher alcohols such as 3,5,5-trimethyl hexanol and isodecanol, and higher acids and amines such as n-nonoic acid and 3,5,5-trimethylhexylamine. Particularly
 25 effective are mixtures of alcohols with complex-forming carbonyl compounds, such as isopropanol mixed with acetylacetone. In the second process it is of particular advantage to use the lower alcohols, e.g. methanol and
 30 ethanol, because of their cheapness. By means of methods such as the above low ash contents, e.g. below 0.02% by weight, may readily be obtained.

The copolymer compositions of our invention may be manufactured into sheet, rod, films and filaments or fibres by known methods. They may be made into articles of many kinds by a wide variety of known techniques, e.g. injection moulding, compression
 40 moulding, extrusion, blow moulding and rotational casting. Those of relatively high transparency have many applications in the packaging field, e.g. in packaging films or bottles. The mechanical properties of the copolymer
 45 compounds can to a certain extent be tailored to the application for which they are required; flexibility is increased by increasing the proportion of second component in the composition. Higher 1-olefines (e.g. decene-1) increase flexibility more than lower 1-olefines (e.g. butene-1).

The copolymer compositions of our invention may be compounded with additives of all kinds, e.g. heat and light stabilisers, fillers, antioxidants, antistatic agents, carbon black, pigments, flame retardant materials, slip agents. They may also be blended with other polymers, e.g. low density polythene, high density polythene, polypropylene and butyl
 60 rubber.

In the following Examples the compression mouldings are made in the following way:

The dried polymer obtained is placed in a
 65 2 × 2 × 1/16" preform and compression

moulded under a pressure of 20 tons/square inch for five minutes. The temperature used in compression moulding is 250°C. The moulding is then removed from the press and either immediately quenched by plunging in cold water or allowed to cool slowly in the press. It is found that the mean spherulite sizes of the copolymers of our invention do not generally vary very much (frequently by not more than a factor of about 2) according to how they are moulded, unless the moulding is deliberately cooled very slowly or held for a long time at a temperature close below the melting point.

The polymer compositions were compression moulded because this is a simple way of fabricating small polymer samples, but in many cases it will be possible to obtain better transparency in articles prepared by a melt homogenisation process, e.g. extrusion.

Average spherulite sizes are measured by photomicrography of the specimen using polarised light. The mean spherulite size is taken from measurements of the diameters of about 100 spherulites. Light transmissions were measured by ASTM Test D.1746—62T and hazes by ASTM Test D.1003—61, the specimens being immersed in dimethyl phthalate to remove surface scattering.

In these Examples, low temperature brittle point was measured by ASTM Test D.746—57T, using unnotched specimens of dimensions 2.0 × 0.25 × 0.16 cm. bent round a mandrel of 0.4 cm. radius by a hammer travelling at 7 feet per second.

Flexural modulus was determined after ageing for 14 days by a simple beam bending method at 20°C.

The titanium chloride used in the Examples was prepared by reaction of TiCl₄ and aluminium ethyl sesquichloride in a purified hydrocarbon fraction. A solution of the sesquichloride in this diluent was added gradually drop by drop, with stirring, to a solution of TiCl₄ in the same diluent over a period of several hours, the temperature being held at 0°C. The molar ratio of total aluminium to titanium was approximately 1.6. The resulting slurry containing TiCl₃ was subsequently heated for a period at 95°C. It was introduced into the polymerisation vessel in the form of a slurry in hydrocarbon.

The following Examples illustrate our invention but do not limit it in any way.

EXAMPLES 1—3

A catalyst comprising titanium trichloride (prepared in the manner previously described) and aluminium diethyl monochloride in a molar ratio of 1 mole of the former to 2 of the latter was suspended under air- and water-free conditions in a purified high-boiling petrol fraction at 30°C and 9.5 moles propylene per mole titanium trichloride were added. When polymerisation was substantially com-

plete the temperature was raised to 60°C and 2.8 moles 3-methyl-butene per mole titanium trichloride were added and left to polymerise at this temperature for 18 hours. Samples of the pretreated catalyst so formed were used to polymerise mixtures of propylene and octene-1. To 500 mls high-boiling paraffin fraction was added an aliquot of slurry containing 6 millimoles aluminium diethyl chloride and 3 millimoles titanium trichloride together with preformed polymer. Propylene was fed at atmospheric pressure for two hours and octene-1 was added steadily over the

same period. The temperature of polymerisation was 40°C. At the end of two hours a mixture of dry isopropanol and acetylacetone was added and the temperature raised to 60°C. After a period at this temperature the slurry was filtered and the polymer washed with dry isopropanol until the filtrate was colourless. A comparative experiment A was carried out in an exactly similar manner, but using no octene-1. Compression mouldings were made, and 3-methylbutene-1 and octene-1 contents measured by infra-red analysis; results are shown in Table I.

TABLE I

Example or Comparative Experiment	Octene ml. added	% 3-methyl-butene-1 by weight	% octene by weight	Quench cooled Spherulite sizes microns		
				Maximum	Mean	Minimum
A	Nil	3	Nil	4	2	<1
1	10	4	5	2	1	<1
2	20	3	13	<1	<1	<1
3	40	3	17	<1	<1	<1

EXAMPLE 4

A titanium, trichloride catalyst was pre-treated as in Examples 1—3, but using 60 moles propylene and 12 moles of 3-methyl-butene per mole titanium trichloride.

An aliquot of this pretreated catalyst containing 10 millimoles titanium trichloride and

20 millimoles aluminium diethyl chloride were placed in 1200 mls hydrocarbon diluent under air- and water-free conditions. Propylene was fed at atmospheric pressure for 3½ hours at 60°C, octene-1 (in total 80 mls) being added steadily throughout. The resulting polymer was worked up as in Examples 1—3.

A comparative experiment B was carried out in identical manner except that no octene-1 was added. Mechanical and optical properties

TABLE II

Example or Comparative Experiment	Flexural modulus (psi $\times 10^3$)	Low Temp. Brittle Point ($^{\circ}$ C.)	Quenched Spherulite Size			Light Transmission (%)		Haze	% 3-methyl-butene-1	% octene-1
			Max.	Av. (microns)	Min.	Quenched	Slow cooled			
B	1.94	13.0	<1	<1	<1	20	5	64	5	0
4	0.78	-7.7	<1	<1	<1	64	32	8	5	6

EXAMPLE 5

A titanium trichloride catalyst was pre-treated as in Examples 1—3, but using 30 moles propylene and 6 moles 3-methylbutene-1 per mole titanium trichloride.

An aliquot of the pretreated catalyst slurry containing 15 millimoles titanium trichloride (and other ingredients in proportion) was added under air- and water-free conditions to 3 litres hydrocarbon diluent in a 5-litre autoclave. Propylene was added at 60 $^{\circ}$ C until a conversion of 120 grams polymer/litre of diluent had formed; octene-1 (in total 100 mls)

was added steadily over the same period. The resulting polymer was worked up as in Examples 1—3.

Three comparative experiments, C, D and E were also carried out. In comparative experiments C and D the step of pretreating the catalyst was omitted, and in experiments C and E no octene-1 was added to the polymerisation. Otherwise conditions were identical with those used in the sample. Optical and mechanical properties of quenched compression mouldings are shown in Table III.

TABLE III

Example or Comparative Experiment	Flexural modulus (psi $\times 10^6$)	Low Temp. Brittle Point (°C.)	Quenched Spherulite Size			Light Transmis- sion (%)	% by weight 3-methyl- butene-2	% by weight octene-1
			Max.	Av. (microns)	Min.			
C	1.91	2.4	30	20	10	0.62	Nil	Nil
D	0.97	-11.7	25	15	5	3.0	Nil.	5
E	1.85	-2.6	1	<1	<1	26.0	0.5	Nil
5	1.05	-9.0	<1	<1	<1	40.0	0.5	3

EXAMPLE 6

Example 4 was repeated exactly, except that 80 ml hexene-1, instead of 80 ml octene-1, was added during the propylene feed. A quenched compression moulding of the resulting polymer contained 5% by weight 3-methyl butene-1, 8% by weight hexene-1, had a light transmission of 57%, a mean spherulite size of $<1\mu$, a low temperature brittle point of -13.1°C and a flexural modulus of 0.504×10^5 psi.

EXAMPLES 7-17

In one litre of purified hydrocarbon diluent, under Ziegler conditions, were placed a catalyst as specified in Table IV comprising 12 millimoles titanium trichloride and 36 millimoles aluminium diethyl chloride. The temperature was raised to 50°C and propylene and butene-1 were passed into the vessel. The partial pressures of propylene and butene-1 were varied, but their sum in each case was approximately 960 mm.Hg. Polymerisation was continued at 50°C for about 6 hours. De-

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TABLE IV

Example or Comparative Experiment	Catalyst Type	Butene-1 content weight %	3-methyl- butene-1 content weight %	Melt flow index*	Mouldings quenched		Mouldings cooled in press	
					% Transmission	Spherulite Size (μ) Mean	% Transmission	Spherulite Size (μ) Mean
F	A	0	1.4	0.08	32	1	1.7	5
G	A	0	1.2	1.7	32	<1	0.4	6
H	A	0	1.4	24.0	28	2	0.8	5
I	X	14	0	0.6	3	10	—	—
7	B	15	1.6	0.7	57	<1	19	2
8	B	14	1.5	6.4	53	<1	5.8	3
9	B	12	1.9	11	59	<1	11	2
10	B	15	1.8	18	50	<1	9	3
11	B	14	1.7	30	54	<1	9	2
J	X	23	0	1.8	15	3	—	—
12	A	24	1.7	1.9	44	<1	5	2
13	A	23	1.8	9.5	50	<1	8	2
14	A	24	1.6	16.5	44	<1	12	2
15	A	22	1.7	38.0	23	<1	12	3
16	C	11	1.0	0.9	66	1	22	2
17	D	20	2.4	3.2	69	<1	—	—

* 190°C/10 kg. 1% Stabiliser

ashing as carried out as in Examples 1—3; the polymer so obtained (generally about 100—150 grams) was made into quenched and slow-cooled compression mouldings. Properties of these and other details are shown in Table IV. Comparative experiments F to J were also carried out in similar manner, but in comparative experiments F to H no butene-1 was present, while in comparative experiments I and J a pretreated catalyst was not used. Details of the catalysts given in Table IV are as follows:

Catalyst A was prepared by passing propylene into titanium trichloride and aluminium diethyl chloride (molar ratio of the former to the latter being 1:3) under Ziegler conditions for about 3 hours at 50°C. 3-Methyl-butene-1 was then added and polymerisation took place for a further 30 hours at 50°C. The 12 millimole aliquot of titanium trichloride used in the main polymerisation had formed thereon 3.1 grams polypropylene and 2.0 grams poly-3-methyl-butene-1.

Catalyst B was prepared in the same way as *Catalyst A*, but was found to contain 3.1 grams polypropylene and 2.2 grams poly-3-methyl-butene-1 in each 12 millimole aliquot of titanium trichloride.

Catalyst C was prepared in the same way as *Catalyst A*, but was found to contain 4.9 grams polypropylene and 1.6 grams poly-3-methyl-butene-1 in each 12 millimole aliquot of titanium trichloride.

Catalyst D was prepared in the same way as *Catalyst A* except that instead of the propylene treatment hexene-1 was initially polymerised for 6 hours at 50°C. It was found to contain 8.2 grams polyhexene and 1.8 grams poly-3-methyl-butene-1 in each 12 millimole aliquot of titanium trichloride.

Catalyst X was not subjected to any polymerising pretreatment.

EXAMPLE 18

A pretreated catalyst was prepared by mixing 10 millimoles titanium trichloride with 20 millimoles aluminium diethyl chloride under polymerising conditions at 30°C and treating with 3-methyl butene-1 so that 60 millimoles 3-methyl butene-1 are polymerised on the catalyst.

The catalyst so obtained was suspended in 1200 mls. of high boiling purified petrol diluent and a mixture of propylene (160 gms.) and hexene-1 polymerised at 40°C. The resulting polymer was worked up as in Examples 1—3; 160 grams of a product were obtained which was shown by infra-red analysis to contain 2% by weight 3-methyl butene-1 and 13% by weight hexene-1. Compression mouldings had the following properties: quenched, 75% light transmission, 11% haze, means spherulite size $>1\mu$; slow-cooled, 54% light transmission, 31% haze, mean spherulite size 2μ .

EXAMPLES 19—24

A pretreated catalyst was prepared as in Example 18. It was suspended in 1200 mls. of purified high boiling petrol diluent, and used to polymerise a mixture of propylene (160 grams) and hexene-1 (various amounts) at 60°C. Both monomers were added steadily throughout polymerisation. The resulting polymer was worked up as in Examples 1—3 and made into compression mouldings, both quenched and slow-cooled. Analysis and various tests were carried out, the results of which are shown in Table V.

TABLE V

Example (or Comparative Experiment)	Hexene-1 added ml.	Solubles recovered from diluent (%w/w on monomer)	M.F.I. (190/10)	Packing Density g./l.	Flexural Modulus (psi \times 10^{-5})	Low Temper- ature Brittle Point °C.	Light Transmission		Haze		% by weight	
							Slow Cooled %	Quenched %	Slow Cooled %	Quenched %	3-methyl butene-1	Hexene-1
19	40	5.42	5.5	435	0.86	-8	41	65	58	19	3	7
20	20	4.00	7.0	461	1.03	-3	34	65	57	21	4	4
21	20	6.13	6.5	480	1.20	-4.1	33	60	—	26	3	3
22	10	4.95	4.7	476	1.45	-0.2	32	52	—	38	4	2
23	5	4.82	3.1	458	1.65	+3.7	19	52	73	37	3	1
24	2.5	3.90	2.4	456	2.02	+4.4	20	44	72	44	4	<0.5
K	Nil	5.21	2.5	455	2.05	+1.9	9	40	—	44	3	Nil

EXAMPLE 25

A mixture of 95 ml. of a slurry of titanium trichloride containing 100 millimoles titanium trichloride in a purified high-boiling alkane diluent and 185 ml. of 1.6 molar aluminum diethyl chloride in the same diluent (300 millimoles aluminum diethyl chloride) was stirred at 50°C over 4 hours while propylene (67 ml. of liquid, 40 g.) was absorbed. The unreacted propylene was removed in vacuum and 30 ml. (20 g.) of 3-methyl pentene-1 added to the reaction, which was then stirred at 50°C for 72 hours. The excess monomer was removed in vacuum.

In the catalyst slurry produced 1 millimole of titanium trichloride bore 5.5 millimoles of polymerised propylene and 2.15 millimoles of polymerised 3-methyl pentene-1.

A portion of the above catalyst containing 12 millimoles titanium trichloride (45 ml. of slurry) was used to copolymerise propylene and 1-butene at 50°C according to the method of Examples 7—17. Over a period of 5 hours the total monomer feed was 373 ml. of liquid propylene and 50 ml. of liquid 1-butene. The product was isolated as in Examples 1—3 to yield 149.3 g. of copolymer containing 15% by weight of butene and 1.5% by weight of

3-methyl pentene-1. A sample was milled at 190°C and then quench moulded from 250°C to give a 1/16" plaque having a light transmission of 54%.

WHAT WE CLAIM IS:—

1. A solid polymer moulding composition comprising a copolymer of propylene, said composition comprising at least 55% by weight propylene monomer units, monomer units of a second component, which is a linear 1-olefine having from 4 to 18 carbon atoms, in an amount of up to 35% by weight and having dispersed throughout the composition polymer units of a third component, which is an α -olefine whereof the homopolymer has a crystalline melting point above 180°C, present in an amount of up to 10% by weight.
2. A composition as claimed in claim 1 which contains at least 2% by weight of the second component.
3. A composition as claimed in claim 2 in which the second component is butene-1, hexene-1 or octene-1.
4. A composition as claimed in either of claims 2 or 3 in which the third component is such that its homopolymer has a crystalline melting point above 260°C.
5. A composition as claimed in claim 4 in which the third component is 3-methyl butene-1 or 3-methyl pentene-1.
6. A composition as claimed in any of claims 2 to 5 which when quench compression moulded has a mean spherulite size of below 1 μ .
7. A composition as claimed in any of claims 2 to 6 which when quench moulded in 1/16" section shows a light transmission of at least 40%.
8. A composition as claimed in any of claims 2 to 8 which also contains ethylene monomer units.
9. A composition as claimed in any of claims 2 to 8 substantially as described with reference to any of Examples 1 to 17.
10. A composition as claimed in any of claims 2 to 8 substantially as hereinbefore described, particularly with reference to any of Examples 18 to 25.
11. A shaped article, including a sheet, rod, film, filament or fibre, made from a composition as claimed in any of claims 2 to 9 or 34.
12. A process for making the composition claimed in claim 1 which comprises bringing propylene, the second component and the third component into contact with an α -olefine polymerisation catalyst and recovering a solid copolymer composition comprising at least 55% by weight of propylene monomer units, monomer units of the second component in an amount of up to 35% by weight and polymer units of the third component in an amount of up to 10% by weight.
13. A process for making a composition

as claimed in any of claims 2 to 8 which comprises bringing propylene, the second component and the third component into contact with an α -olefine polymerisation catalyst and recovering a solid copolymer composition comprising at least 55% by weight of propylene monomer units, from 2 to 35% by weight of monomer units of the second component and polymer units of the third component in an amount of up to 10% by weight.

14. A process as claimed in claim 13 in which the α -olefine polymerisation catalyst is a stereospecific catalyst (as hereinbefore defined).

15. A process as claimed in claim 14 in which the stereospecific catalyst comprises titanium trichloride activated by an organo-aluminium compound.

16. A process as claimed in claim 14 in which the titanium trichloride is obtained by reducing titanium tetrachloride with aluminium alkyl sesquichloride in a purified alkane medium with stirring in an inert atmosphere at 0°C.

17. A process as claimed in claim 16 in which the reduction is carried out by adding the aluminium alkyl sesquichloride in alkane solution gradually to an alkane solution of the titanium tetrachloride.

18. A process as claimed in any of claims 15 to 17 in which the organo-aluminium compound is dialkyl aluminium chloride.

19. A process as claimed in claim 13 in which the third component is polymerised before any substantial quantity of any other monomer has been polymerised.

20. A process as claimed in claim 13 wherein the third component is polymerised subsequent to the polymerisation of another monomer.

21. A process as claimed in claim 20 in which propylene, the second component and the third component are all present together in the polymerisation zone and polymerisation is carried out for a time sufficient to polymerise substantially all the propylene and the second component and subsequently to polymerise at least some of the third component.

22. A process as claimed in claim 19 wherein the third component is polymerised in a separate preliminary stage.

23. A process as claimed in claim 20 wherein initially propylene or second component is polymerised in small amount, subsequently the third component is polymerised and thereafter the bulk of the propylene is polymerised.

24. A process as claimed in claim 23 wherein the initial polymerisation of propylene or second component and the subsequent polymerisation of third component are carried out in a separate preliminary stage.

25. A process as claimed in any of claims 14 to 24 in which one monomer is initially

homopolymerised in the absence of any other monomer until at least 1% by weight of the final polymer product has been formed.

5 26. A process as claimed in claim 25 in which the temperature of the initial homopolymerisation is at or below 30°C.

10 27. A process as claimed in either of claims 25 or 26 in which up to 10% by weight of the final polymer product is formed in the initial homopolymerisation.

15 28. A process as claimed in any of claims 25 to 27 wherein initially propylene is homopolymerised and thereafter the third component is polymerised in the presence of a high concentration of catalyst, diluent is then added to lower the catalyst concentration and subsequently propylene and the second component are polymerised.

20 29. A process as claimed in any of claims 13 to 28 in which the polymer composition

obtained is deashed under substantially anhydrous conditions using dry reagents.

30. A process as claimed in claim 29 in which a mixture of alcohol and acetylacetone is used as deashing agent.

31. A process as claimed in any of claims 13 to 30 in which hydrogen is added during polymerisation.

32. A process as claimed in any of claims 13 to 31 substantially as described with reference to any of Examples 1 to 17.

33. A process as claimed in any of claims 12 to 31 substantially as hereinbefore described, particularly with reference to Examples 18 to 25.

34. A polymer composition made by the process claimed in any of claims 13 to 33.

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